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FAILURE ANALYSIS OF THE LITHIUM BATTERY: A STUDY OF THE  
HEADER DEPOSIT ON THE CELL TOP AND DIFFUSION WITHIN  
THE ELECTRODE GLASS SEAL USING NUCLEAR MICROANALYSIS AND  
FTIR SPECTROSCOPY

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## INTRODUCTION

The Solid Rocket Booster Range Safety System (SRBRSS) uses a lithium/poly-carbon monofluoride primary battery as a source of electrical power. The battery is manufactured by the Eagle Picher Industries. After cell fabrication and activation some battery cells have shown self discharge. One possible source of this cell discharge has been suggested to be the formation and growth of a conducting crystallized chemical compound across the glass bead insulator, electrically shorting the glass bead to the casing. This laboratory has begun an analysis of this compound, the glass seal holding the cathode into place, and the cell electrolyte, using Fast Fourier Transform Infrared (FFTIR) Analysis, Rutherford Backscattering Spectroscopy (RBS), and Nuclear Reaction Microanalysis. Preliminary measurements have confirmed the existence of lithium, nitrogen, fluorine, and oxygen on a reddish-brown deposit covering parts of the glass seal holding the positive electrode in place.

Cells using Li metal electrodes, have many advantages over conventional primary batteries (5). One principal disadvantage of using Li batteries on a commercial basis would be the environmental impact of the fluorocarbon material. Another would be the relatively high expense of (CF)<sub>n</sub>.

The overall cell reaction and the electrolyte chemicals are described in (1) and (6).

## EXPERIMENTS

Fast Fourier Infrared Spectroscopy (FFTIR) was used to analyze the organics present on the glass seal surface and the electrolyte material. These experiments were performed in the laboratory of Dr. James Thompson of Alabama A&M University. The Rutherford Backscattering Spectroscopy (RBS) and Nuclear Reaction Microanalysis were used to semiquantitatively analyze the atomic compositions of the glass surface and within the glass seal. These experiments were performed in an accelerator in the James Foster Radiation Center, directed by Dr. Daryush Ila, of Alabama A&M University.

This problem has been previously studied extensively by NASA scientists (3). Scattering Electron Microscopy (SEM) was done on the electrodes, glass seals, and headers, to study the higher atomic weight elements ( $Z > 19$ ). These results suggested the presence of the following elements: magnesium, silicon, sulfur, potassium, barium, iron, nickel, arsenic, and chlorine. They also suggested that the problem of cell discharge/shorting is in the manufacturing design. It was suggested that if the company manufacturing the batteries would take more cautionary measures that this problem would probably be eliminated:

- (A) isolate the NASA batteries from impurities during the manufacturing process. NASA batteries, apparently, are prepared in an environment which does not exclude impurities such as Cl<sup>-</sup>.
- (B) changing the glass seal. Some have suggested using a "Zeigler-Type" seal, to replace the present glass seal.

Others at NASA (2a) have suggested that because of the many chemicals present in the cell system (electrodes, casings, electrolytes, separators, etc.), it will be extremely difficult to analyze all of the possible chemical reactions that take place. This is especially true for LDEF batteries, due to the extended contact of the cells' chemicals with one another.

#### NUCLEAR MICROANALYSIS

Nuclear microanalyses were performed on the cell header deposit and the glass seal. (see figs. 1&2). Fluorine was detected in the glass. There is little doubt that it came from the cathode material. Lithium was also detected. It is uncertain if the Li present was from the electrode or simply from the glass itself, since one of the components of the glass is Li. More quantitative studies need to be performed. A "significant amount" of lithium and fluorine were present in the reddish-brown deposit on the glass surface.

As previously mentioned, there are many possible chemical reactions that could take place within the LDEF cells, given the composition of the cell components and the length of time (6 years) they have been in close contact with each other.

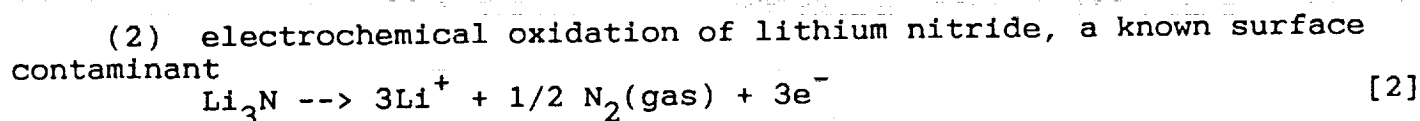
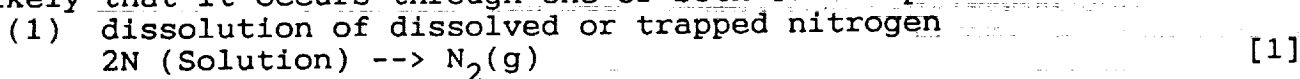
#### FFTIR

These spectra have not given conclusive information. Preliminary tests do not confirm the presence of DMSO in the electrolyte through the reduction of DMSI, as this investigator suspects. More work needs to be done. It has been suggested that Nuclear Magnetic Studies (NMR) could give the kind of information that is needed to support the author's hypothesis concerning the electrolyte.

#### DISCUSSION

It is interesting that the reddish-brown material on the surface of the glass seal has the same physical appearance as  $\text{Li}_3\text{N}$  (4). The source of the Li could have been the electrode or the electrolyte. Nitrogen appears to be a natural contaminant of Li metal. "The solid solubility of nitrogen in lithium at the eutectic temperature is 0.024 mol percent at  $180.24^\circ\text{C}$ . This high solubility of nitrogen suggests that in lithium batteries, some nitrogen is expected to be evolved during discharge, unless the gas is scrupulously excluded from the lithium. Attempts to remove nitrogen from Li by filtration have suggested that once this metal has been saturated with nitrogen, impurity levels below 0.08 mol percent would be difficult to achieve" (4). Studies on polycrystalline  $\text{Li}_3\text{N}$  showed it to be a good conductor of Li<sup>+</sup> at moderate temperatures.

Nitrogen gas,  $\text{N}_2$ , has been observed when Li cells discharge (4). It is likely that it occurs through one or both of the possible mechanisms:



This latter reaction is catalyzed by moisture.

It has already been suggested by members of this laboratory that the discharge/ shorting problem somehow involves the glass seal. Preliminary RBS results confirm the presence of Li in the glass. Since Li is also one of the ions already present in the glass, it cannot be stated at this point whether it came from "somewhere outside of the glass" or not. More quantitative studies need to be made to confirm this point.

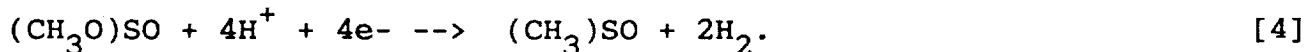
There are, however, many possible paths for electrochemical reactions to occur between the Li electrode and the glass.

In a damp environment, the Li electrode develops a grayish-black tarnish which progresses to a white powder of LiOH:

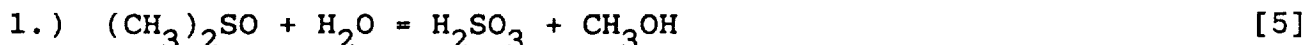


Visual observations suggest that some of this material is also found on the header.

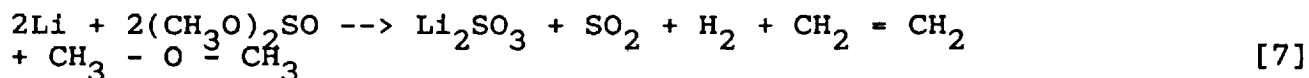
The organic solvent in the electrolyte is DMSI, dimethyl sulfite. It is speculated that some of this substance is reduced to DMSO, dimethyl sulfoxide. There are reports which suggest that Li is more soluble in DMSO than in DMSI. It is suspected that some of the DMSI is being converted into DMSO through the following possible mechanism:



The DMSO would then dissolve some of the Li metal. One possible mechanism for this process is as follows:



There is also speculation that the following reaction takes place between DMSI and the Li electrode:



All of these hypotheses should be further tested using NMR studies on the electrolyte mixture.

#### PROJECTED RESEARCH

It is clear why one NASA researcher was moved to suggest that the problem of chemically analyzing the Li cells is at best an extremely difficult one. At Alabama A&M, work has begun to successfully identify the chemical components of the glass seal and the header deposit. Some of the findings support their initial hypothesis concerning a discharge mechanism for the lithium batteries. This analysis, however, needs

quantitative research in order to completely characterize the cell chemistry, thus, to find the reason behind the shorting.

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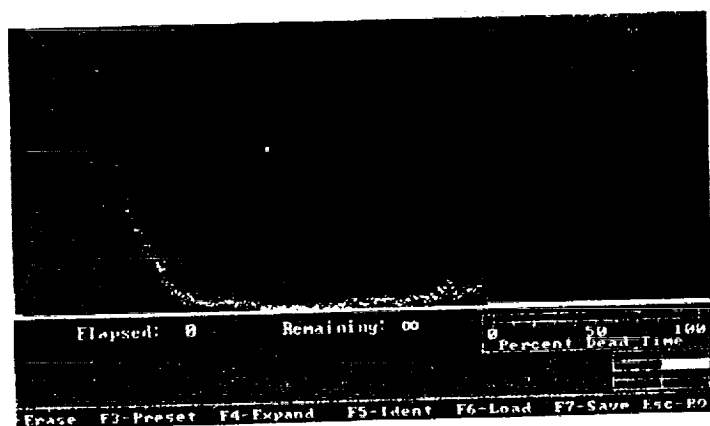


Figure 1

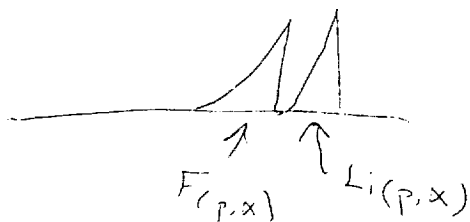


Figure 1: ALPHA Particles Spectrum  
Header Material Indicates the presence of Lithium and Fluorine.

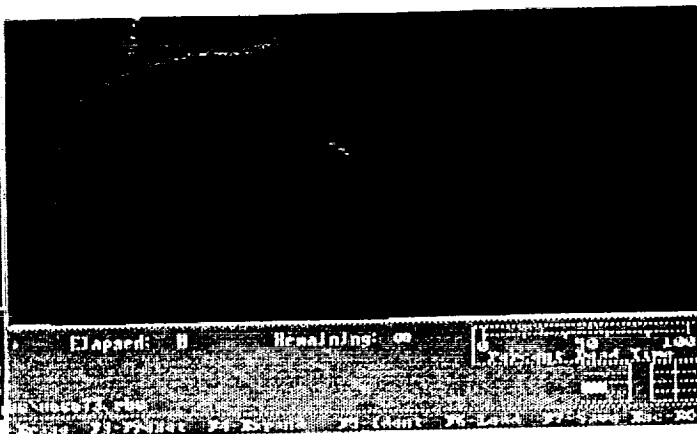


Figure 2



Figure 2: RBS Spectrum (1.614 MEV Protons)  
Header Deposit indicates the presence of Nitrogen, Oxygen, Fluorine.